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The Crystal Structure of $Sc_2Ru_5B_4$*

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The crystal structure of $Sc_2Ru_5B_4$ has been determined by single-crystal X-ray analysis. $Sc_2Ru_5B_4$ crystallizes in the primitive monoclinic space group $P2/m$ with $a = 9.983(6)$, $b = 8.486(4)$, $c = 3.0001(3)$ Å, $\gamma = 90.01(7)°$, $Z = 2$. Deviations from the orthorhombic space group $Pbam\text{-}D_{2h}^{9}$ are small but significant. Intensity measurements were obtained from a four-circle diffractometer. The structure was solved by Patterson methods and refined by full matrix least-squares calculation. $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.036$ for an asymmetric set of 863 independent reflections ($|F_0| > 2\sigma(F_0)$). The crystal structure is characterized by two different types of boron atoms: (a) isolated borons B(1) and B(3) in distorted trigonal Ru-prisms with tetrakaidekahedral metal coordination: 6Ru + 3Sc, and (b) boron atoms B(2) and B(4) with a pronounced tendency to form boron pairs (B(2)–B(2) = 1.86 Å, B(4)–B(4) = 1.89 Å); the metal coordination of these boron atoms is 6Ru + 2Sc. Sc atoms have a coordination number of 17 consisting of 10Ru + 2Sc + 5B. The crystal structure of $Sc_2Ru_5B_4$ is a pentagon layer structure (Ru, B atoms) with a $4.3.4.3^2$-secondary layer of Sc atoms. The structure is furthermore related to the structure types of $Ti_3Co_5B_2$ and $CeCo_3B_2$. From powder photographs $Sc_2Os_5B_4$ is isotypic. No superconductivity was observed for $Sc_2(Ru,Os)_5B_4$ down to 1.5 K.

Introduction

A preliminary investigation of the phase equilibria in the system Sc–Ru–B (see Ref. (*1*)) was concerned with the formation and existence of the superconducting phase $ScRu_4B_4$; based on a microprobe analysis of multiphase alloys, Ku *et al.* (Ref. (*1*)) concluded the existence of a new compound labeled as "$ScRu_2B_2$."

A more recent study (Refs. (*2, 3*)) dealt with the magnetic behavior and the crystal chemistry of ternary borides RT_3B_2 whose crystal structures derive from the $CaCu_5$ type by either an ordered metal/boron substitution or by symmetry distortion (R is a rare earth element or U,Th; T = Ru,Os): a new structure type was observed for the corresponding combinations with scandium, and preliminary X-ray data of these new compounds (*2*) suggested a composition slightly richer in scandium and boron as compared to a formula 1 : 3 : 2. Furthermore a close resemblance to the structure type of $CeCo_3B_2$ was indicated from the powder diagrams. With respect to the estimated composition of the new phase, a correspondence to the earlier reported "$ScRu_2B_2$" seemed to be likely, and a detailed determination of the crystal structure became the subject of the present work.

Experimental

Powders of the elements were compacted in steel dies without the use of binder mate-

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* Dedicated to Professor M. J. Sienko in memoriam.

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rials (Sc, filings from ingots, 99.99%, Rare Earth Ltd., Great Britain; Ru and Os powders, 99.9%, Engelhard Ind. Div.; United States of America; B, crystallized, powder, 99.999%, Eagle Picher Ind.). The pellets with a total weight of 0.5–1 g each, and with nominal compositions Sc : Ru(Os) : B = 1 : 3 : 2, 1 : 2,5 : 2 and 1 : 2 : 2 were arc-melted on a water-cooled copper hearth with a nonconsumable, thoriated tungsten electrode under a Ti/Zr-gettered high-purity argon atmosphere. A part of each alloy button was annealed under vacuum (10^{-4} Pa, 72 hr, 1000°C) on a tungsten substrate and radiation-quenched. In both cases (T = Ru,Os) X-ray powder diffraction inspection revealed practically homogeneous and well-crystallized alloys for the nominal compositions $ScT_{2.5}B_2$.

Lattice parameters and standard deviations were evaluated by a least-squares extrapolation method (*4*) from Guinier powder photographs (obtained at room temperature) using monochromatized Cu$K\alpha$ radiation with an internal standard of 99.9999% pure Ge. Only a small variation was observed for the lattice parameters of the new compounds suggesting the existence of a rather small homogeneity region deriving from a formula $Sc_2T_5B_4$ (T = Ru,Os).

X-Ray powder intensities were recorded by means of a KD-530 microdensitometer.

A small single crystal of $Sc_2Ru_5B_4$ suitable for structure determination was obtained by mechanical fragmentation of an arc-melted sample with nominal composition $Sc_{0.17}Ru_{0.50}B_{0.33}$ (in at.%).

A first inspection of Weissenberg and precession (Laue) photographs (axis [001]) revealed an orthorhombic lattice geometry and the existence of a center of symmetry is displayed from statistical tests. The observation of generally rather weak but significant reflections ($h0l$) for $h = 2n + 1$ and ($0kl$) for $k = 2n + 1$ such as, i.e., (102), (501), (010), (031), (012) etc. results in a small but characteristic deviation from the highest centrosymmetric symmetry $Pbam$-D_{2h}^9. A detailed inspection of the X-ray intensities furthermore revealed the inequality in the intensities of the (hkl) and ($\bar{h}\bar{k}l$) reflections suggesting that the actual symmetry is monoclinic, consistent with the centrosymmetric space group $P2/m(C_{2h}^1$, z-axis unique, $\gamma \sim 90°$). The inequality $I_{(hkl)} \neq I_{(\bar{h}\bar{k}l)}$ is well pronounced in a few cases, ensuring the fact that the deviation from space group D_{2h}^9 is small but significant.

Data collection was performed on a Philips PW-1100 automatic four-circle diffractometer (Austrian Science Research Council, Institute of Mineralogy, Technical University of Vienna) with monochromated Mo$K\alpha$ radiation. Cell parameters were determined from a least-squares refinement of 2θ values of 20 reflections using the program PARAM (X-RAY system (*5*)). The crystallographic data are presented in Table I. A total number of 960 reflections were recorded up to a limit of $\sin \theta/\lambda = 0.7$ Å^{-1}. A set of 863 symmetry-independent intensities was obtained by averaging "centered reflections" only, and all observed intensities were used in the structure determination. An absorption correction was applied for an idealized spherical crystal shape (μR = 1.2 (*6*)).

All samples were tested for superconductivity in an ac-induction equipment (see Ref. (*7*))—no superconductivity was ob-

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Sc_2Ru_5B_4$ AND $Sc_2Os_5B_4$; SPACE GROUP $P2/m$ (C_{2h}^1—No. 10), Z = 2

$Sc_2Ru_5B_4$	$Sc_2Os_5B_4$
a = 9.9833(64) Å	a = 10.0477(44) Å
b = 8.4859(43) Å	b = 8.5499(48) Å
c = 3.0001(3) Å	c = 3.0216(3) Å
γ = 90.01(7)°	γ = 90.03(8)°
V = 254.16(21) Å^3	V = 259.58(19) Å^3
D_x = 8.34 Mg m^{-3}	D_x = 13.87 Mg m^{-3}
μ(Mo$K\alpha$) = 15.6 mm^{-1}	μ(Mo$K\alpha$) = 119.5 mm^{-1}

TABLE II

ATOMIC AND THERMAL PARAMETERS FOR $Sc_2Ru_5B_4$ ($P2/m$, UNIQUE AXIS c, NO. 10)

Atom	Site	x	y	z	Occ.	U (Å^2)	U_{11}	U_{22}	U_{33}	U_{12}
2 Sc 1	2n	0.3178(2)	0.1582(2)	1/2	1.0	1.10(8)	1.39(12)	1.15(12)	1.41(13)	0.21(8)
2 Sc 2	2n	0.1814(2)	0.6577(2)	1/2	1.0	1.28(8)	1.42(12)	1.24(13)	1.15(12)	0.03(8)
2 Ru 1	2m	0.0477(1)	0.1606(1)	0	1.00(2)	0.98(5)	1.06(5)	1.04(5)	1.21(6)	0.12(3)
2 Ru 2	2m	0.4526(1)	0.6603(1)	0	0.97(2)	1.00(5)	0.89(5)	0.90(5)	1.11(6)	0.10(3)
2 Ru 3	2m	0.2619(1)	0.4044(1)	0	0.98(2)	0.93(5)	0.98(5)	0.94(5)	1.18(6)	0.16(3)
2 Ru 4	2m	0.2385(1)	0.9041(1)	0	1.00(1)	1.07(5)	0.91(5)	1.10(5)	1.19(6)	0.09(3)
1 Ru 5	1d	0	1/2	0	0.99(1)	0.80(6)	0.83(7)	1.01(7)	1.16(8)	0.19(4)
1 Ru 6	1c	1/2	0	0	0.99(1)	1.15(6)	0.87(7)	0.89(7)	1.16(8)	0.05(4)
2 B 1	2n	0.1030(12)	0.3493(17)	1/2	1.0	1.05(22)				
2 B 2	2n	0.4107(14)	0.4686(15)	1/2	1.0	1.24(23)				
2 B 3	2n	0.4011(11)	0.8462(15)	1/2	1.0	1.16(19)				
2 B 4	2n	0.0903(21)	0.9660(22)	1/2	1.0	1.37(36)				

Note. Standard deviations are in parentheses; isotropic temperature factors are expressed as $T = \exp[-2\pi^2 \cdot 10^{-2} U\,(2\sin\theta/\lambda)^2]$; anisotropic thermal factors are of the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots) \cdot 10^{-2}]$; by symmetry $U_{13} = U_{23} = 0$.

served down to 1.5 K (see also Ref. (*1*) for "$ScRu_2B_2$").

Structure Determination

Two formula units of $Sc_2Ru_5B_4$ were derived from a comparison of the atomic volumes with the volume of the unit cell assuming a space filling of 70%. The obvious correspondence between the structure factors $F_{(h,k,l)} \approx F_{(h,k,l+2)}$ suggested an atomic arrangement in layers at a distance of $c/2$. Due to the small deviations of the actual crystal symmetry from the orthorhombic space group D_{2h}^9, a first structure model was derived in orthorhombic symmetry: the prominent peaks of a three-dimensional Patterson map were consistent with 4Ru in $4g$ (0.0474(1), 0.1603(1), 0); 4Ru in $4g$ (0.2617(1), 0.4042(1), 0), and 2Ru in $2c$ (0, $\frac{1}{2}$, 0); the position of the 4 Sc atoms in $4h$ (0.3183(3), 0.1576(3), $\frac{1}{2}$) was found from an electron density map. The boron sites were clearly resolved from a difference Fourier map $F_0 - F_{Sc,Ru}$: 4B in $4h$ (0.1025(17), 0.3506(20), $\frac{1}{2}$), and 4B in $4h$ (0.4089(22), 0.4660(26), $\frac{1}{2}$).

This structure model was transferred into the monoclinic space group $P2/m$ and refined with the full matrix least-squares program CRYLSQ (X-RAY system (*5*)). Hartree Fock scattering factors were used for Sc, Ru, and the boron atoms (*8*). The anomalous dispersion correction (Sc, Ru) was taken from Cromer and Liberman (*9*), and structure factors were furthermore corrected for isotropic secondary extinction. Weights $w_i = 1/(\sigma_i(F))^2$ were attributed to all observed reflections; different weighing schemes had no significant influence on the R-value obtained. A refinement of the occupancy of the Ru-positions did not result in a significant deviation from a full occupation. The final R-value, calculated with isotropic extinction and anisotropic thermal parameters was $R = 0.036$. (with isotropic thermal parameters $R = 0.040$). At this point a difference map $F_0 - F_c$ was featureless. The final positional and thermal parameters are given in Table II; atomic distances up to 4.0 Å are presented in Table III. A table of F_0 and F_c is available from the author. Using the single-crystal parameters in Table II, agreement is found between calculated and

TABLE III

Interatomic Distances in $Sc_2Ru_5B_4$ (<4.0 Å)

Sc 1–2 Sc 1	3.000(0)	Ru 1–2 Sc 1	3.086(2)	Ru 4–2 Sc 1	2.743(2)	B 1–1 Sc 1	2.689(14)
–2 Ru 1	3.086(2)	–2 Sc 2	3.140(2)	–2 Sc 2	2.636(2)	–1 Sc 2	2.732(14)
–2 Ru 2	3.143(2)	–2 Ru 1	3.000(0)	–1 Ru 1	2.892(1)	–1 Sc 2	2.840(13)
–2 Ru 3	2.632(2)	–1 Ru 1	2.887(1)	–1 Ru 1	2.910(1)	–2 Ru 1	2.263(11)
–2 Ru 4	2.743(2)	–1 Ru 3	2.975(1)	–1 Ru 2	2.975(1)	–2 Ru 3	2.233(10)
–2 Ru 6	2.713(2)	–1 Ru 4	2.892(1)	–2 Ru 4	3.000(0)	–2 Ru 5	2.223(10)
–1 B 1	2.689(14)	–1 Ru 4	2.910(1)	–1 Ru 6	2.735(1)		
–1 B 2	2.793(13)	–1 Ru 5	2.919(1)	–2 B 3	2.264(9)	B 2–1 Sc 1	2.793(13)
–1 B 2	2.775(13)	–2 B 1	2.263(11)	–2 B 4	2.171(15)	–1 Sc 2	2.796(14)
–1 B 3	2.807(12)	–2 B 4	2.271(15)			–2 Ru 2	2.252(10)
–1 B 4	2.796(21)	–2 B 4	2.303(15)	Ru 5–4 Sc 2	2.706(2)	–2 Ru 2	2.304(10)
				–2 Ru 1	2.919(1)	–2 Ru 3	2.180(10)
Sc 2–2 Sc 2	3.000(0)	Ru 2–2 Sc 1	3.143(2)	–2 Ru 3	2.738(1)	–1 B 2	1.861(20)
–2 Ru 1	3.140(2)	–2 Sc 2	3.095(2)	–2 Ru 5	3.000(0)		
–2 Ru 2	3.095(2)	–2 Ru 2	3.000(0)	–4 B 1	2.223(10)	B 3–1 Sc 1	2.807(13)
–2 Ru 3	2.742(2)	–1 Ru 2	2.881(1)			–1 Sc 1	2.775(12)
–2 Ru 4	2.636(2)	–1 Ru 3	2.888(1)	Ru 6–4 Sc 1	2.713(2)	–1 Sc 2	2.715(12)
–2 Ru 5	2.706(2)	–1 Ru 3	2.903(1)	–2 Ru 2	2.921(1)	–2 Ru 2	2.237(9)
–1 B 1	2.732(14)	–1 Ru 4	2.975(1)	–2 Ru 4	2.735(1)	–2 Ru 4	2.264(9)
–1 B 1	2.840(13)	–1 Ru 6	2.921(1)	–2 Ru 6	3.000(0)	–2 Ru 6	2.220(9)
–1 B 2	2.796(14)	–2 B 2	2.252(9)	–4 B 3	2.220(9)		
–1 B 3	2.715(12)	–2 B 2	2.304(10)			B 4–1 Sc 1	2.796(21)
–1 B 4	2.770(20)	–2 B 3	2.237(9)			–1 Sc 2	2.770(20)
						–2 Ru 1	2.271(15)
		Ru 3–2 Sc 1	2.632(2)			–2 Ru 1	2.303(15)
		–2 Sc 2	2.742(2)			–2 Ru 4	2.171(15)
		–1 Ru 1	2.975(1)			–1 B 4	1.893(29)
		–1 Ru 2	2.888(1)				
		–1 Ru 2	2.903(1)				
		–2 Ru 3	3.000(0)				
		–1 Ru 5	2.738(1)				
		–2 B 1	2.233(10)				
		–2 B 2	2.180(10)				

observed powder diffraction intensities; as the structure is of a new type, a listing of the reflections for X-ray powder diagram identification is given in Table IV. It is of interest to note, that the refinement of this structure model in the orthorhombic setting of space group D_{2h}^{9} (see above) was as good as $R = 0.06$, despite being unable to account for the small symmetry deviations. Finally, the possible loss of the center of symmetry was investigated by means of a full matrix refinement of the data set in both the noncentrosymmetric monoclinic space groups *Pm* and *P*2; however no visible improvement was obtained with respect to the refinement in *P*2/*m* (Table II), thus the existence of a center of symmetry cannot be excluded.

Isotypic $Sc_2Os_5B_4$

Powder patterns, which were practically single phase have been obtained for a composition Sc : Os : B = 1 : 2.5 : 2 and confirm the existence of a new ternary boride $Sc_2Os_5B_4$. Within the limits of error the powder patterns of the new phase were in-

TABLE IV

POWDER DIFFRACTION DATA FOR $Sc_2Ru_5B_4$ (FOR $\theta < 30°$)

	$10^4 \cdot \sin^2 \theta$		Intensity			$10^4 \cdot \sin^2 \theta$		Intensity	
(*hkl*)	Obs.	Calc.	Obs.	Calc.	(*hkl*)	Obs.	Calc.	Obs.	Calc.
(100)	*	60	*	0	(031)	*	1401	*	0
(010)	*	83	*	0	$(1\bar{3}1)$	1459	1460	96	49.4
$(1\bar{1}0)$	*	142	*	0	(131)		1460		49.5
(110)		142		0	(500)	*	1488	*	0
(200)	240	239	~1.7	1.0	$(3\bar{2}1)$	1524	1524	100	50.5
$(2\bar{1}0)$	320	320	3	1.5	(321)		1525		50.2
(210)		321		1.5	$(2\bar{4}0)$	1557	1556	10	6.1
(020)	329	330	5	5.1	(240)		1557		6.2
$(1\bar{2}0)$	389	389	13	6.0	$(5\bar{1}0)$	1570	1571	~1.5	1.1
(120)		389		6.0	(510)		1571		1.1
(300)	*	536	*	0	(401)	1612	1612	53	55.6
$(2\bar{2}0)$	*	568	*	0.1	$(2\bar{3}1)$	*	1639	*	0
(220)		568		0.1	(213)		1639		0
(310)	*	618	*	0.3	$(4\bar{3}0)$	1694	1694	12	1.2
$(3\bar{1}0)$		618		0.3	(430)		1694		1.3
(001)	660	659	85	86.0	$(4\bar{1}1)$		1694		4.4
(101)	*	719	*	0	(411)		1694		4.5
(030)	*	742	*	0	$(5\bar{2}0)$	*	1818	*	0.2
(011)		742		0	(520)		1818		0.2
$(1\bar{3}0)$	802	801	52	25.5	$(3\bar{4}0)$	*	1854	*	0.1
(130)		801		25.4	(340)		1854		0.1
$(1\bar{1}1)$		801		0.7	$(3\bar{3}1)$	1937– –1941	1936	20	4.6
(111)		801		0.8	(331)		1937		4.5
$(3\bar{2}0)$	866	865	63	33.1	$(4\bar{2}1)$		1941		5.0
(320)		866		33.0	(421)		1941		5.1
(201)	897	897	11	10.4	(041)	1977	1978	3	3.6
(400)	954	953	38	40.2	$(1\bar{4}1)$	2038	2037	8	3.8
$(2\bar{3}0)$	981	980	23	0.3	(141)		2037		4.0
(230)		980		0.3	(050)	*	2060	*	0
$(2\bar{1}1)$		980		11.1	$(1\bar{5}0)$	*	2119	*	0.4
(211)		980		11.1	(150)		2119		0.4
(021)	989	989	8	8.8	(600)	*	2143	*	0.7
$(4\bar{1}0)$	1036	1035	46	23.5	(501)	*	2148	*	0
(410)		1035		23.4	$(2\bar{4}1)$	2215	2215	5	2.5
$(1\bar{2}1)$	1050	1048	46	24.5	(241)		2216		2.5
(121)		1048		24.2	$(6\bar{1}0)$	2230	2225	~2	0.6
(301)	*	1195	*	0	(610)		2226		0.6
$(2\bar{2}1)$	1225	1227	5	2.5	$(5\bar{3}0)$		2229		0.8
(221)		1227		2.5	(530)		2230		0.8
$(3\bar{3}0)$	1277	1277	54	22.4	$(5\bar{1}1)$		2230		0
(330)		1277		22.3	(511)		2230		0
$(3\bar{1}1)$		1277		6.4	$(4\bar{4}0)$	2271	2270	~1	0.7
(311)		1277		6.7	(440)		2271		0.6
$(4\bar{2}0)$	1283	1282	8	4.6	$(2\bar{5}0)$	2299	2298	~1	0.6
(420)		1282		4.7	(250)		2298		0.6
(040)	1317	1318	11	12.8	$(4\bar{3}1)$	2355	2353	~2	1.0
$(1\bar{4}0)$	1377	1378	25	12.4	(431)		2354		0.9
(140)		1378		12.4	$(6\bar{2}0)$	*	2472	*	0

Note. Meaning of asterisk: Not observed. Material: Sc(18)Ru(45)B(37), arc-melted. Method: powder X-ray diffraction in a Guinier camera, Cu$K\alpha_1$ radiation (99.9999% Ge standard). The intensity I is normalized to the strongest reflection with I = 100. Lattice and atom parameters are from Tables I and II.

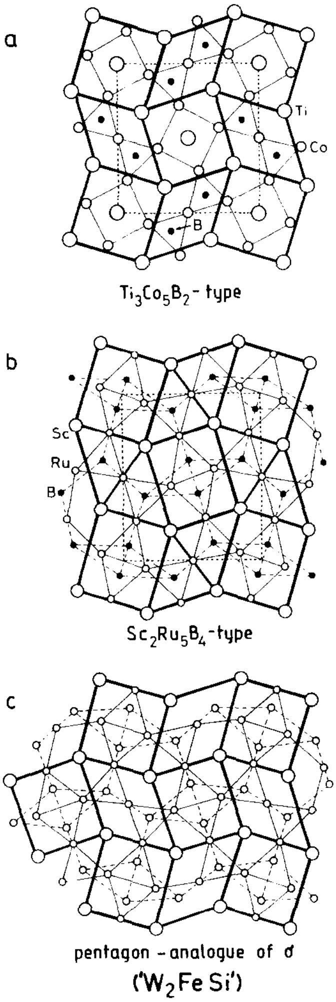

FIG. 1. Comparison of the crystal structures of (a) $Ti_3Co_5B_2$ (Ref. (*11*)), (b) $Sc_2Ru_5B_4$, and (c) of the pentagon analog of the σ-phase ("W_2FeSi," see Refs. (*12–15*)). All structures are projected along [001]. (a) $Ti_3Co_5B_2$: Co atoms are in $z = 0$; Ti,B atoms in $z = 1/2$. (b) $Sc_2Ru_5B_4$: Ru-pentagon triangle nets are in $z = 0$, B and Sc atoms are in $z = 1/2$. (c) "W_2FeSi": atoms connected by thick solid lines are in $z = 1/4$ and 3/4 thin solid lines are in $z = 0$, and dashed lines in $z = 1/2$ (for comparison with $Sc_2Ru_5B_4$ the unit cell of "W_2FeSi" is shifted by (1/2, 1/2, 1/2) with respect to the original setting given in (*15*)).

dexed completely on the basis of an orthorhombic unit cell, however Guinier photographs do show a remarkable amount of slightly diffuse reflections which is indicative for the first stages of a monoclinic lattice distortion. Using the atomic parameters derived for $Sc_2Ru_5B_4$ (Table II), the observed and calculated intensities show fine agreement. Thus from composition, lattice parameters (Table I) and as far as X-ray powder intensity data are concerned, $Sc_2Os_5B_4$ is concluded to be a structure analog of $Sc_2Ru_5B_4$, bearing in mind that a decision about the very small monoclinic symmetry distortion can be obtained from detailed single-crystal studies only.

Description of the Structure and Discussion

Figure 1b is a graphical representation of the crystal structure of $Sc_2Ru_5B_4$ projected down the *c*-axis. The different coordination figures have been derived from the interatomic distances in Table III. Ruthenium atoms form planar pentagon–triangle layers with a stacking sequence AAA ($z = 0, 1, \ldots$). The so-formed pentagonal Ru-prisms are connected along edges and consist of CN14-(4Sc + 6Ru + 4B, Ru 3,4,5,6) and CN17-(4Sc + 7Ru + 6B, Ru 1,2) atoms. A secondary $3^2.4.3.4$-net of Sc atoms in $z = 1/2$ is arranged between the Ru-main layers; the Sc atoms form infinite chains along the center lines of the (nonregular) pentagonal Ru-prisms, and with five additional boron atoms outside the rectangular faces of the prism the coordination of each Sc atom is 2Sc +10Ru + 5B. The triangular prismatic interstitial voids of the Ru-sublattice are occupied by boron atoms. As seen from Fig. 1b and Table III, boron atoms B1 and B3 are isolated in tetrakaidekahedral metal coordination of 6Ru + 3Sc; the reduced metal coordination of B2 and B4 atoms (6Ru + 2Sc) is compensated by the tendency of these boron atoms to form boron–boron contacts (boron pairs). A weak bonding however is inferred from the observed distances B2–B2 = 1.86 Å and B4–B4 = 1.89

Å as compared to typical covalent boron bond lengths of 1.76–1.82 Å.

The appearance of isolated borons and boron pairs in $Sc_2Ru_5B_4$ is in good accordance to the classification of binary and ternary boride structures by means of their different types of boron aggregation as a function of the ratio of transition metal to boron T: B (see, i.e., Ref. (*10*)). From this classification scheme a ratio T: B ≈ 1.5 was generally found to be characteristic for the formation of boron pairs, whereas for metal-rich borides the occurrence of isolated boron atoms is natural. A remarkable resemblance exists between the structure types of $Sc_2Ru_5B_4$ and the $CeCo_3B_2$ or $CaCu_5$ types, where the large rare earth atoms with a high coordination number CN = 12Co + 2Ce + 6B are found to be located in the center of a hexagonal column formed by triangular transition metal prisms (3.6.3.6 kagomé transition metal layer with a 3^6-secondary layer of RE atoms). Due to the reduced coordination number of the much smaller scandium atoms, the number of the surrounding trigonal prisms is decreased to the formation of a similar but pentagonal column. The replacement of hexagons by pentagons results in the combination of two triangular metal prisms which share a common prism face and as a consequence allow for the formation of a boron pair. A formal substitution of this boron pair by a metal atom generates the structure type of $Ti_3Co_5B_2$ (Ref. (*11*)), which is further obtained as a topochemical combination of $CeCo_3B_2$-type units with intermetallic clusters of the CsCl type:

$$Ti_3Co_5B_2 = Ti_2(Ti)Co_5B_2 \rightarrow Sc_2(B_2)Ru_5B_2 = Sc_2Ru_5B_4$$

$$Ti_3Co_5B_2 = TiCo_3B_2\ (\text{``}CeCo_3B_2\text{-type''}) + 2TiCo\ (\text{``CsCl-type''}).$$

The interesting crystal-chemical relation between these two structure types $Sc_2Ru_5B_4$ and $Ti_3Co_5B_2$ is documented in Figs. 1a,b.

The interatomic distances in $Sc_2Ru_5B_4$ (see Table III) display a rather weak scandium–boron but a strong ruthenium–boron interaction ($R_{Ru} + R_B = 2.22$ Å); Ru–Ru distances on the average exceed the sum of their Goldschmidt radii ($R_{Ru} = 1.34$ Å) by more than 5%. This behavior corresponds to the general observations regarding bonding in different distortion derivatives of the $CeCo_3B_2$-type structure in combination with rare earth and alkaline earth metals (Ref. (*10*)).

All boron atoms in $Sc_2Ru_5B_4$ are in $z = 1/2$ and formally constitute an arrangement of face-connected pentagons and triangles; the pentagons being centered by Sc atoms ($z = 1/2$, Fig. 1b). There is however no direct boron–boron bonding within the boron pentagons. Despite $Sc_2Ru_5B_4$ certainly should not be grouped among the so-called tetrahedrally close-packed structures, some aspects of the layer arrangement resemble the tetrahedrally close-packed structures in particular the pentagon-analog of the σ-phase (Fig. 1c) that was earlier derived by Frank and Kasper (*13*) as a hypothetical structure type and later discussed by Shoemaker and Shoemaker (*12*); as pointed out by Shoemaker (*14*) the structure of $W_6(Fe_{0.465}Si_{0.465}W_{0.07})_7$ or "W_2FeSi" (*15*) was found to be a representative of this "pentagon-sigma" type. The main difference between these formally related structure types, i.e., the pentagon $\sigma(W_6(W,Fe,Si)_7)$ and the $Sc_2Ru_5B_4$ type is found in the different position of the $4.3.4.3^2$ secondary "layers" which are in $z = 1/4$, 3/4 for pentagon σ but in $z = 1/2$ for $Sc_2Ru_5B_4$; it is this difference which finally constitutes a completely altered bonding situation for both structure types. The formal relationship however is documented in Figs. 1b,c.

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